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1. TITLE

Analysis of CS and CS precursor (2-chlorobenzaldehyde) in varied matrixes by Gas Chromatography Mass Spectrometry (GC/MS)

2. AUTHORS

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3. KEYWORDS

CS, 2-chlorobenzaldehyde, soil, wipes, air filter, GC/MS, quantitative.

4. REVISION HISTORY

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5. CONTACT OFFICE

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6. PURPOSE AND APPLICATION

This method is used to quantify CS and 2-chlorobenzaldehyde in air (using glass fiber filters), soil and wipe samples by gas chromatography mass spectrometry (GC/MS) analysis.

6.1 **LINEARITY / ANALYTE CONCENTRATION RANGE** The calibration curve for SCAN analysis is linear and ranges from 10.0 µg/mL to 100.0 µg/mL. This is equivalent to concentrations of 0.02 mg/m^3 to 0.40 mg/m^3 in 480 liters of an air matrix. A calibration range of 1.0 to 10 µg/mL is used for the analysis of wipe and soil samples. This is equivalent to concentrations of 0.050 µg/g to 0.50 µg/g in 20 grams of soil and 0.063 ng/in^2 to 0.630 ng/in^2 on a 16 in^2 wipe area.

6.2 **SAMPLE MATRICES AND INTERFERENCES** The sample matrix is environmental air/soil/wipe samples. Analyses conducted indicated that interference's do not exist regarding target compounds.

6.3 **THROUGHPUT** Approximately twelve (12) samples can be analyzed in an eight (8) hour period.

6.4 **DETECTION LIMIT** The method detection limits (MDL) for CS is 0.0037 mg/m^3 in air samples, 0.072 µg/g in soil samples and 0.090 ng/in^2 in wipe samples. The MDL for 2-chlorobenzaldehyde is 0.040 µg/g in soil samples and 0.051 ng/in^2 in wipe samples. This method cannot be used to determine 2-chlorobenzaldehyde concentrations in air because glass fiber filter air sampling is not applicable to 2-chlorobenzaldehyde.

7. RISK AND SAFETY ASSESSMENT

Low risks to the analyst are associated with this method provided the proper safety precautions are strictly adhered to. Wearing of lab coat, safety glasses and nitrile gloves is required when handling any sample associated with the chemical agent. Solvents used in this method pose a risk to the analyst and must be handled with care inside of a well-ventilated hood. Chemical agent must be handled with extreme caution and only in an approved hood. Guidelines for handling solvents and agent materiel can be found in WI-090 (Sample Receipt and Handling) and in ERDECR 40-3 (Chemical Hygiene Plan).

8. SCIENTIFIC BASIS

This method is based on collecting a known volume of air (over a period of time with a glass fiber filter/air pump apparatus), soil or wiping a known surface area with a wipe. Then extracting the filter/soil/wipe with two 20 mL aliquots of methylene chloride that is concentrated to 1.0 mL with a turbovap. The concentrated methylene chloride is analyzed by GC/MSD to determine CS/2-chlorobezaldehyde concentrations using an external standard method of quantitation.

9. TRAINING

The analyst must meet the qualification requirements specified in Edgewood C/B FAC operating procedure OP-180. The analyst should have a thorough knowledge of

operating a Hewlett Packard (Agilent) HP5890 Series II Plus GC with a 5972 Mass Selective Detector and ChemStation software. Personnel performing sample preparation activities must have completed training in Basic Chemical Sample Preparation Techniques as defined by the Edgewood, C/B FAC quality system.

10. APPARATUS

10.1 INSTRUMENTATION

The instrumentation required includes a Hewlett-Packard (Agilent) 5890 Series II Plus GC equipped with a 5972-Mass Selective Detector. The column used is a HP-5MS fused silica column (5% Phenyl Methyl Silicone – 30 M x 0.25 mm-id x 0.25 um film thickness).

10.2 GLASSWARE, MISCELLANEOUS EQUIPMENT AND SUPPLIES

GC crimp top autoinjector vials, 2 mL (Hewlett-Packard (Agilent), Cat. No. 5181-3376)*
GC vial caps, 11 mm septa (Hewlett-Packard (Agilent), Cat. No. 5181-1210)*
Injection Port liner, deactivated single taper, 4 mm (Hewlett-Packard (Agilent), Cat. No. 5062-3587)*
Hewlett-Packard (Agilent) HP-5MS fused silica column, 30 M x 0.25 mm i.d. x .25 um film (Hewlett-Packard (Agilent), Cat. No. 190115-433)*
Pasteur pipettes (VWR, Cat. No. 14673-010)*
Pipette, 100-1000 µL (Rainin, Cat. No. E2-1000)*
Pipette tips (Rainin, Cat. No. RT-200)*
Syringes, 10 µL, 25 µL, 50 µL, 100 µL, 250 µL, 500 µL, 1000 µL (VWR)*
Volumetric flask 10 mL with stopper (Kimble Glass, Co.)*
Safety Glasses (e.g., VWR, cat. # 33002-049)*
Lab Coat (e.g., VWR, cat. # 10836-420)*
Nitrile Gloves (e.g., VWR, cat. # 32891-804)*
Glass vial with solid cap, Teflon™ liner, 7 ml (e.g., Supelco, cat. # 2-7341)*
Pasteur pipettes, 5 ¾ inches (e.g., VWR, cat. # 14673-010)*
Rubber bulbs for Pasteur pipettes (e.g., VWR, cat. # 56310-240)*
Timer (e.g., VWR, cat. # 62344-585)*
Glass Fiber Filters 1.0 micron (e.g., VWR)*
* or equivalent
Source Details
Supelco, Inc, Supelco Park, Bellefonte, PA 16823
VWR Scientific, 1430 Waukegan Rd, McGaw Park, IL 60085

10.3 CHEMICALS / STANDARDS

10.3.1 Reagents / chemicals

Methylene Chloride, CAS# 75-09-2, Reagent Grade or equivalent
Acetone, CAS# 7217-25-6,Pesticide grade or equivalent

10.3.2 Standards

(CS) o-chlorobenzylidene malonitrile, CAS# 2698-41-1
2-chlorobenzaldehyde, CAS# 89-98-5

10.3.5 Calibration Stock Solution:

10.3.5.1 Weight out 30 mg of CS and 2-chlorobenzaldehyde.
10.3.5.2 Mix and dilute to the mark of a 10 mL volumetric flask with Methylene Chloride. The nominal concentration is 3000 µg/mL.

10.3.6 Calibration standards:

10.3.6.1 100 µg/ml: 333 µL of the Calibration Stock Solution (3000 µg/mL) / 10 mL volumetric flask. Mix and dilute to the mark with methylene chloride.
10.3.6.2 75 µg/ml: 250 µL of the Calibration Stock Solution (3000 µg/mL) / 10 mL volumetric flask. Mix and dilute to the mark with methylene chloride.
10.3.6.3 50 µg/ml: 167 µL of the Calibration Stock Solution (3000 µg/mL) / 10 mL volumetric flask. Mix and dilute to the mark with methylene chloride.
10.3.6.4 25 µg/ml: 83 µL of the Calibration Stock Solution (3000 µg/mL) / 10 mL volumetric flask. Mix and dilute to the mark with methylene chloride.
10.3.6.5 10 µg/ml: 33 µL of the Calibration Stock Solution (3000 µg/mL) / 10 mL volumetric flask. Mix and dilute to the mark with methylene chloride.
10.3.6.6 Solutions are stable for 3 months.

10.3.7 Matrix spike and Laboratory Control Solutions:

50 µg/mL: 420 µL of Calibration Stock Solution of 3.0 mg/mL CS / 2-chlorobenzaldehyde / 25 mL of Acetone.

11. PROCEDURE

11.1 OPERATION PARAMETERS

Gas Chromatograph:

Injection volume	1 µL splitless injection
Column flow	1.0 mL/min (7.1 psi at 40°C.), vacuum comp. on
Split vent	closed for 1.00 min.
Split vent flow	55 mL/min

Injection port temp	250°C.
Detector temp	280°C.
Oven program	40°C. hold 1.0 min
Rate 1	10°C./min
Final temp	280°C. hold 10.0 min
Final hold	2.0 min
Run time	35 min
5972 Mass Spectrometer:	
Transfer line temp:	280°C
Total ion scan range:	35-560 amu

SCAN Analysis:

Compound	Quantitation-Ion	Qualifier-Ions
CS	153.00	188.00, 126.00, 136.95
2-chlorobenzaldehyde	139.00	11.00,140.00

11.2 SAMPLE PREPARATION

11.2.1 Place glass fiber filter/20 gram soil/wipe in a clean 200 mL beaker.

11.2.2 Add 20 mL of methylene chloride and stir for 5 min.

11.2.3 Pour 20 mL of methylene chloride into a turbovap tube.

11.2.4 Repeat step 11.2.2 and 11.2.3 with another 20 mL of methylene chloride.

11.2.5 Concentrate the methylene chloride to 1.0 mL using a turbovap.

11.2.9 Using a disposable pipette, transfer the methylene chloride from the turbovap tube to a 2 ml GC vial.

11.2.10 Submit the sample for GC/MS analysis. With each batch of 20 or fewer samples, the following quality assurance samples are also prepared:

11.2.11 Method Blank: One glass fiber filter/20 grams reagent grade soil/clean wipe. Extracted along with the samples following the above procedure.

11.2.12 Matrix and Matrix Spike Duplicate: One glass fiber filter/20 grams reagent grade soil/clean wipe spiked with the target compound.

11.2.13 Laboratory Control Standard: One glass fiber filter/20 grams reagent grade soil/clean wipe spiked with the target compound.

11.3 SAMPLE ANALYSIS

A 1.0 µL sample is analyzed using a Hewlett-Packard (Agilent) 5890 Series II Plus Gas Chromatograph equipped with an autoinjector and a Mass Selective Detector. The analysis is conducted in the total ion scan mode according to the instrument conditions described in Section 11.1.

11.4 CORRECTIVE PROCEDURES

If the calibration fails or the calibration check standards do not pass criteria, the samples analyzed prior to the failed check standard will be re-analyzed. For all other instrumental problems, refer to the owner's operating manual.

12.0 CALCULATION, CALIBRATION AND DOCUMENTATION

12.1 CALCULATION

Concentrations and calculations of the analyte of interest will be based on a 5- point calibration curve with external standards. Appropriate factors (amount of air sampled) will be taken into account in these calculations.

$$\text{Relative Response Factor} = \frac{\text{Area (compound)}}{\text{Concentration (Compound)}}$$

$$\text{Concentration} = \frac{\text{Area (compound)}}{\text{Relative Response Factor}}$$

12.2 BLANK DETERMINATION AND CALIBRATIONS

Appropriate reagent and matrix blanks are analyzed along with each set of samples. A 5-point calibration will be initiated prior to analyzing any sample. The origin (point 0,0) is included in the calibration curve. Figure 1 provides an example of the typical output from a calibration standard containing 5.0 µg/mL of CS/2-Chlorobenzaldehyde.

12.3 QUALITATIVE ANALYSIS

12.3.1 Qualitative identification of compound determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction with at least 3 characteristic ions in a reference mass spectrum. The following criteria must be met:

12.3.1.1 The intensities of the compound's characteristic extracted ion profiles maximize in the same scan or within one scan of each other.

12.3.1.2 The relative retention time (RRT) of the sample component is within +/- 0.06 RRT units of the RRT of the standard component.

12.3.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum.

12.4 STANDARDS, CONTROLS, SPIKES, AND VALIDATION PROGRAMS

12.4.1 GC/MSD Tune

As an instrumental quality control measure, prior to each day's analysis a Standard Spectra AutoTune will be performed. Also a 1 µL injection of hexachlorobenzene (HCB) at 1 µg/mL will be run to monitor instrument signal to noise ratio and performance.

12.4.2 Continuing calibration check

A mid-point calibration standard is analyzed with each batch of samples and after every 10 samples, however, another calibration standard may be substituted. If the calibration check standard does not pass criteria (+/- 25%), the samples analyzed prior to the failed check standard shall be reanalyzed. If two consecutive check standards fail, corrective maintenance action must be taken. The instrument is re-calibrated and the samples reanalyzed. For other instrument problems, consult the operating manual for trouble shooting help.

12.4.3 Laboratory Control Spike/Matrix spike / Matrix spike duplicate

With each set of 20 or fewer samples, a Laboratory Control Sample, matrix spike and matrix spike duplicate is analyzed. Each is spiked with 100 µg/mL CS and 2-chlorobenzaldehyde as part of the extraction procedure. Recoveries must fall within 20 to 150% of spiking levels and relative percent differences must be within 25%. The recovery and percent RSD are recorded on Edgewood C/B FAC form FR-0901 until enough data is accumulated to calculate control limits in accordance with work instruction WI-200. Figure 2 provides an example of GC/MSD chromatogram of a matrix spike containing 0.125 µg/g of CS/2-chlorobenzaldehyde.

12.4.4 Method Validation

12.4.3.1 Spike Recovery Study

For the spike recovery study for CS, three clean glass fiber filter were spiked with CS at 50.0 µg/mL (0.10 mg/m^3 in 480 liters of air) and three at 25.0 µg/mL (0.05 mg/m^3 in 480 liters of air) and extracted. The 1.0 mL methylene chloride extract from each was submitted for GC/MSD analysis. (See Table 1 for summary of results.)

For the spike recovery study for 2-chlorobenzaldehyde, three reagent grade soil samples were spiked with 2-chlorobenzaldehyde at 0.250 µg/g and three at 0.500 µg/g and extracted. The 1.0 mL methylene chloride extract from each was submitted for GC/MSD analysis. (See Table 2 for summary of results.)

12.4.3.2 MDL Study

A method detection limit (MDL) was performed as described in Chapter 1 of EPA SW-846 (Reference 7). Seven replicates of the matrix spike containing Lewisite at a concentration three to five times higher than the estimated detection limit was analyzed. The MDL was determined by multiplying the appropriate one-sided 99% t-statistic (for 7 measurements 3.14) by the standard deviation of the replicate measurements. The estimated quantitation limit (EQL) was equal to 5 to 10 times the MDL. (See Table 3 and 4 for summary of MDL results.)

TABLE 1

PRECISION AND ACCURACY DATA: CS (glass fiber filter)

AMOUNT SPIKED (mg/m3)	AMOUNT RECOVERED (mg/m3)	PERCENT RECOVERY	STD. DEV.	%RSD	N
0.100	0.093	93	0.0025	2.5	3
0.050	0.045	90	0.0003	0.6	3

TABLE 2

PRECISION AND ACCURACY DATA: 2-chlorobenzaldehyde (Soil)

AMOUNT SPIKED (µg/g)	AMOUNT RECOVERED (µg/g)	PERCENT RECOVERY	STD. DEV.	%RSD	N
0.125	0.141	113	0.0169	8.9	3
0.250	0.269	108	0.0612	17.8	3

TABLE 3

METHOD DETECTION LIMIT DATA: CS

MATRIX	AMOUNT RECOVERED	STANDARD DEVIATION	T-STATISTIC N=7	METHOD DETECTION LIMIT
Air mg/m3	0.018	0.0012	7	0.0037
Soil µg/g	0.458	0.0229	7	0.072
Wipe ng/ in^2	0.573	0.0289	7	0.090

TABLE 4

METHOD DETECTION LIMIT DATA: 2-chlorobenzaldehyde

MATRIX	AMOUNT RECOVERED	STANDARD DEVIATION	T-STATISTIC N=7	METHOD DETECTION LIMIT
Soil µg/g	0.054	0.012	7	0.040
Wipe ng/ in^2	0.068	0.016	7	0.051

13.0 STATEMENT OF ANALYTICAL RESULT:

The results of the determination of target analytes are reported in mg/m3 for air, µg/g for soil and ng/ in^2 for wipes with a maximum of three (3) significant figures. Results of the recoveries of the matrix spike and the matrix spike duplicate are reported. Results are reported as "nd" when no detectable signal or a signal below the MDL are obtained.

14. REFERENCES

1. Army Materiel Command Treaty Laboratory Analytical Support, Standing Operating Procedure CR2-ISP002 (1997), U. S. Army Materiel Command Treaty Laboratory, Chemical and Biological Defense Command, Edgewood, MD.

2. Amendment One to Standing Operating Procedure CR2-ISP002, Army Materiel Command Treaty Laboratory Analytical Support (1997), U. S. Army Materiel Command Treaty Laboratory, Chemical and Biological Defense Command, Edgewood, MD.

3. The Army Toxic Chemical Agent Safety Program, Army Regulation 385-61 (1997), Headquarters, Department of the Army, Washington, DC.

4. Toxic Chemical Agent Safety Standards, Department of the Army Pamphlet 385-61 (1997), Headquarters, Department of the Army, Washington, DC.

5. Chemical Accident or Incident Response and assistance (CAIRA) Operations, Department of the Army Pamphlet 50-6 (1995), Headquarters, Department of the Army, Washington, DC.

6. Nuclear and Chemical Weapons and Materiel: Chemical Surety, Army Regulation 50-6 (1995), Headquarters, Department of the Army, Washington, DC.

7. U.S. EPA SW 846.

Figure 1. Example of GC/MSD chromatogram of a calibration standard containing 5.0 µg/mL of 2-Chlorobenzaldehyde and CS.

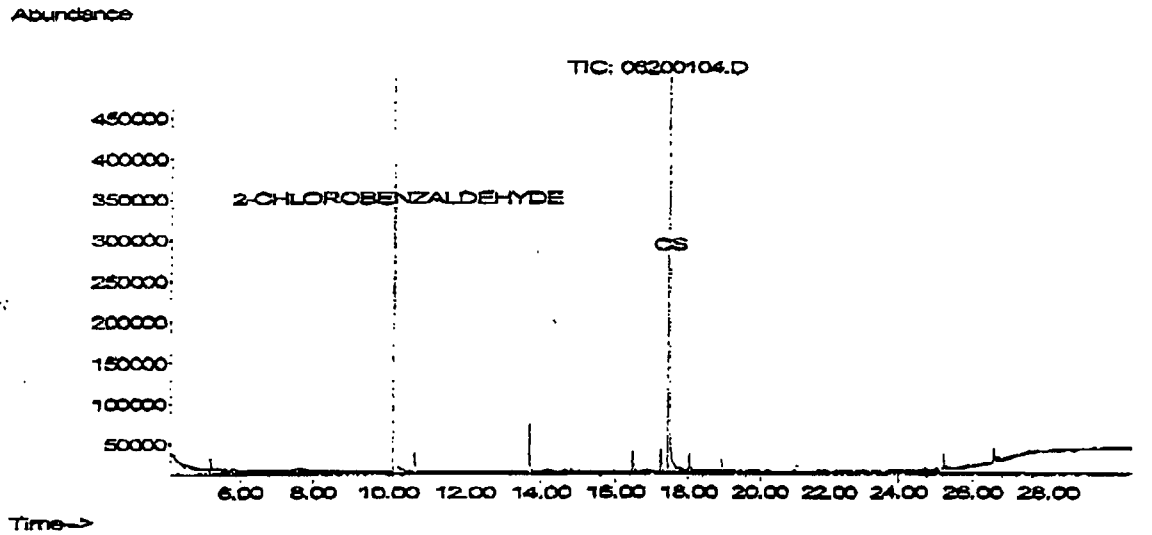
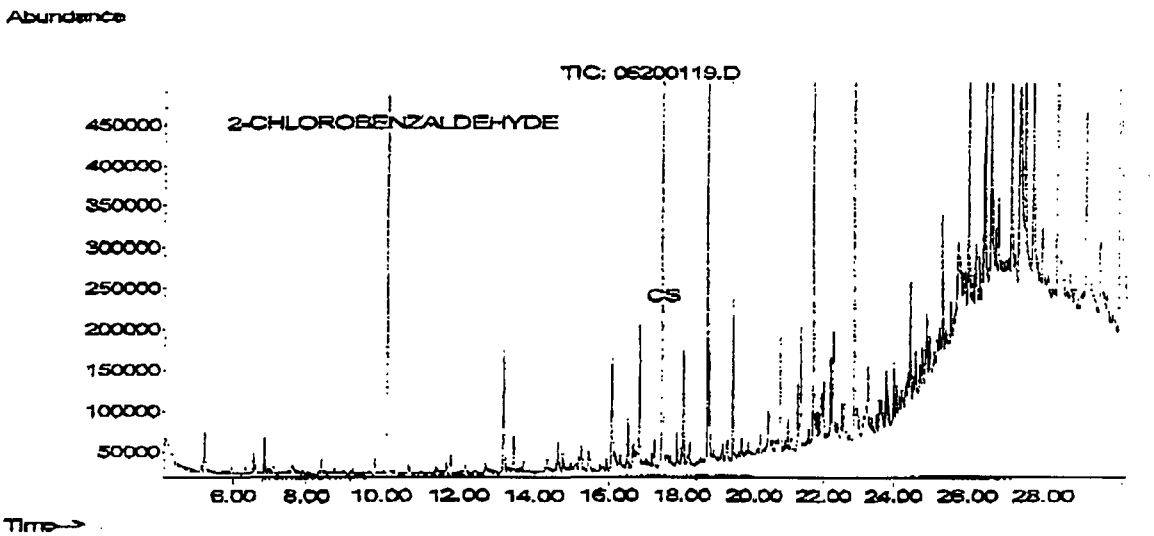


Figure 2. Example of GC/MSD chromatogram of a matrix spike sample containing 0.125 µg/g of 2-Chlorobenzaldehyde and CS.



Revision History

Rev. No.	Description of Revision	Approval/Date
0	Original	*(9 May 01)* MARY F. DRUMMOND
1	Changed title to add "2-Chlorobenzaldehyde" and additional matrices. Updated sections 6.1, 6.2 and 6.4 to reflect change in title. Updated sections 10.3.5 and 10.3.7 to add 2-Chlorobenzaldehyde Added SCAN analysis information for 2-Chlorobenzaldehyde to section 11.1. Changed the reference to figure 1 in section 12.2. Updated sections 12.4.3, 12.4.4 and 13 for the change in method scope.	6-21-01 MARY F. DRUMMOND